Titanium and Copper Oxide Based Catalysts for the *In-situ* Reactions of Methanation and Desulfurization in the Removal of Sour Gases from Simulated Natural Gas

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ABSTRACT

The objective of this novel catalyst development is to achieve both low temperature and high conversion of sour gases. Supported mixed metal oxide catalysts were prepared by impregnating the catalysts on alumina beads for the *in-situ* reactions of H_2S desulfurization and CO_2 methanation from room temperature up to 200°C. The results showed that the 100% conversion of H_2S to elemental sulfur for all of the potential catalysts was achieved at 100°C. However, methanation of CO_2 in the presence of H_2S yielded 0.4% CH_4 over Fe/ Zn/ Cu/ Ti-Al_2O_3 catalyst and 0.7% CH_4 over Fe/ Zn/ Cu-Al_2O_3 catalyst at maximum studied temperature of 200°C. XPS results indicated that spinel compounds of $CuFe_2O_4$ and Fe_3O_4 act as the active sites on the Fe/ Zn/ Cu-Al_2O_3 and Fe/ Zn/ Cu/ Ti-Al_2O_3 catalysts. The appearance of Fe^{3+}-OH on Fe/ Zn/ Cu/ Ti-Al_2O_3 catalyst increased its H_2S desulfurization activity. N_2 adsorption-desorption analysis illustrated that 34% of the surface area of Fe/ Zn/ Cu-Al_2O_3 catalyst was reduced while Fe/ Zn/ Cu/ Ti-Al_2O_3 catalyst showed reduction of 17% after catalytic testing, which indicated the deactivation of the catalysts resulted from sulfur poisoning.

| Titanium | copper | methanation | desulfurization | natural gas |

1. Introduction

Crude natural gas is categorized as sour gas due to the contamination of carbon dioxide (CO_2) and hydrogen sulfide (H_2S). These corrosive elements may deteriorate the pipeline systems and become a safety hazard and also contribute to the environmental issue. Recently, the removal of these sour gases via chemical conversion techniques becomes the most promising technique. The catalysts for the CO_2 methanation have been extensively studied because of their application in the conversion of CO_2 gas to produce methane, which is the major component in natural gas. However, the presence of H_2S in certain industrial processes is known to cause poisoning of the commercial nickel based catalyst.

The essential requirement for the correct selection of the oxide system is its ability to accept and to activate CO_2 and H_2S. The acid nature of CO_2 and H_2S necessitates the employment of a catalytic system with basic properties. The acid and redox properties of transition metal oxides could be changed by adding other oxides [1]. Investigation done by Wang *et al.* [2] found that the adsorption strength of CO_2 is controlled by the Lewis basicity of a catalyst, d-band center of the metal surface, charge transfer from the metal surfaces to the chemisorbed CO_2. The major reason for the less reactive of mixed metal oxide is its significantly complexity possibly presence of multiple oxidation states, variable local coordination, coexisting bulk and surface phases as well as different surface termination functionalities such as M-OH, M=O or M-O-M [3]. Metal oxides are less active than metals, but they are stable in catalytic conditions.

Kulshreshtha *et al.* [4] have been reported that Fe-Ti-Sn intermetallics are capable of CO methanation and almost completely converted CO to methane at 323 °C. This investigation concluded that the catalytic activity of the intermetallics is significantly improved by Sn substitution. Later, Pineda *et al.* [5] reported when zinc oxide

and zinc ferrite catalysts were dopped with Cu and Ti, their catalytic performance on H_2S desulfurization process could be increased. The addition of Ti may increase the stability of ZnO towards reducing agent such as H_2. However, the addition of Cu do not affect the stability of catalyst but improve the catalyst performance by changing the surface of the catalyst during calcination and activation process. It has also been found that CO_2 strongly chemisorbs on the Fe (110) surface with the strongest binding energy, whereas CO_2 has moderate strength on the (111) surface of Co, Ni, Rh, Pd with slightly positive binding energies [2]. The selection of support is considered as important since it may influence both the activity and selectivity of the reaction. It has been discovered that the addition of alumina may increase the methanation activity although there is a presence of low concentration of H_2S [6]. Therefore, Al_2O_3 is considered as the support for all the studied catalysts in this research.

Efforts to search for efficient catalyst and to explore new technologies in order to meet the demands of the economical feasibility of *in-situ* reactions of methanation and desulfurization for the purification of natural gas has not been extensively studied. The objective of this novel catalyst development is to achieve both low temperature and high conversion of sour gas. At low temperature, application of the novel catalyst in gas industry is more likely. However, problem arises because exothermic reaction of conversion of CO_2 to CH_4 is unfavorable at low temperature due to its low energy content.

2. Experimental

2.1 Preparation of catalysts

The catalysts were prepared by wet impregnation method. The respective metal nitrate salt was dissolved with minimum amount of distilled water. Mixed catalysts solution was prepared by mixing appropriate amount of metal nitrate salts according to the atomic ratio. Al_2O_3 supported catalyst was prepared by impregnating the catalyst solution on Al_2O_3 beads support for 15 minutes. It was then dried at 80^{o}C for 24 hours and calcined in air at 400^{o}C for 5 hours. To prepare Ti^{4+} sol for the Ti based catalyst, 6 g of polyethylene glycol (PEG) was dissolved with 600 mL of ethanol. After that, 31.8 g diethanolamine (DEA) followed by 85.2 g titanium (IV) isopropoxide ($Ti(iso)_4$) was added when PEG was completely dissolved. 5.4 mL of distilled water was added and stirred for 10 minutes to get a homogeneous solution. Al_2O_3 beads were dipped into the Ti^{4+} sol and then dried in the oven at 80^{o}C for 30 minutes. A mixed metal oxide with Ti sol was prepared by impregnating the resulted Al_2O_3 supported Ti with the respective metal oxide.

2.2 Catalytic activity measurements

The supported catalyst sample was packed into a cylindrical glass tube with diameter of 10 mm and length of 360 mm and was stored in the furnace of the home-built micro reactor. No pretreatment was done prior to beginning the heating experiment. Firstly, screening of the catalytic activity on individual reaction of CO_2 and H_2S conversion was performed under 760 Torr pressure. The conversion of CO_2 was screened from room temperature up to 500 ^{o}C for the conversion of CO_2 and up to 200 ^{o}C for the conversion of H_2S, with temperature rate of 5 ^{o}C/ min. After that, *in-situ* reactions of CO_2 methanation and H_2S desulfurization were performed from room temperature up to 200 ^{o}C. CO_2 and H_2 gases were introduced into the reactor system in a stoichiometric ratio of 1: 4. About 2.5 mL/min H_2S gas was introduced into the gas stream. This composition is similar to the content of sour gases in Malaysian natural gas, which is 5 % of H_2S and 20 % of CO_2. Screening on the produced gas stream was done by using FTIR analysis. Percentage conversion of CO_2 and H_2S was obtained by calculating the peak area of their respective stretching band relative to the peak area of the gas during calibration without catalyst. Off line Gas Chromatography analysis was done on the product gas to determine the selectivity and yield of CH_4 gas due to the low sensitivity of FTIR towards stretching band of CH_4.

2.3 Characterization of catalysts

2.3.1 X-rays Photoelectron Spectroscopy

The potential catalysts were characterized by using Kratos instrument XSAM HS surface analysis spectrometer with Mg Kα x-rays source (1253.6 eV). Sample was introduced into the spectrometer in flowing argon atmosphere, and evaporated at least 6×10^{9} Torr before spectrum was recorded. The spectrum was taken at 10 mA and 14 kV energy source at 2 sweeps.

2.3.2 Nitrogen Adsorption Analysis

The N_2 adsorption-desorption isotherms for the catalysts were measured by Micromeritics ASAP 2010. All samples were evacuated at 120 ^{o}C prior to the measurement. The specific surface area was calculated using the BET method. The total pore volume was determined at a relative pressure of $P/P_o = 0.99$.

3. Results and Discussion

3.1 Catalytic activity measurement

3.1.1 Screening of the catalytic activity using FTIR spectroscopy

A series of Fe/ Zn/ Cu-Al_2O_3 catalyst containing three different ratio was prepared to optimize the copper content towards the catalyst. Table 1 compares the percentage conversion of CO_2 and H_2S catalyzed over Fe/ Zn/ Cu-Al_2O_3 catalyst with different ratios. According to Table 1, the optimum ratio for Al_2O_3 supported Fe/ Zn/ Cu-Al_2O_3 catalyst is 4: 16: 80. 100 % conversion of CO_2 was achieved over this catalyst at reaction temperature of 400 ^{o}C, whereas 100 % H_2S desulfurization was achieved at 100 ^{o}C. Fe/ Zn/ Cu (10:30:60)-Al_2O_3 and Fe/ Zn/ Cu (3: 7: 90)-Al_2O_3 catalysts only showed 98.9 % and 89.9 % conversion of CO_2 respectively, at maximum studied temperature of 500 ^{o}C. It could be seen that high concentration of CuO in the catalyst could increase the amount of surface oxygen on the catalyst surface. Therefore, the percentage conversion of CO_2 over Fe/ Zn/ Cu (3: 7: 90)-Al_2O_3 catalyst was lowered. Relatively, smaller amount of CuO (Fe/ Zn/ Cu = 10: 30: 60) on the catalyst could increase the adsorption of H_2S. However, this catalyst is lack of surface oxygen that needed for desulfurization process as suggested in the previous study [7].

Table 1: Temperature for conversion of CO_2 and H_2S over Al_2O_3 supported Fe/ Zn/ Cu catalysts with different ratios using simulated natural gas.

Catalyst	T_{100} CO_2 [a] (± 0.5°C)	T_{100} H_2S (± 0.5°C)
Fe/ Zn/ Cu (10:30:60)-Al_2O_3	500 (98.9 %)[b]	120
Fe/ Zn/ Cu (4:16:80)-Al_2O_3	400	100
Fe/ Zn/ Cu (3:7:90)-Al_2O_3	500 (89.9 %)[b]	100

[a] Temperature where 100 % conversion was achieved
[b] Value in bracket is the % conversion of CO_2 at maximum studied temperature of 500 ^{o}C

It has been reported by Pineda *et al.* [5] the presence of Ti may increase the H_2S desulfurization process at lower temperature. Therefore, optimization of titanium content towards Fe/ Zn/ Cu/ Ti-Al_2O_3 catalyst was done. Table 2 shows the comparison of percentage conversion of CO_2 and H_2S over Fe/ Zn/ Cu/ Ti-Al_2O_3 catalyst with different ratios.

Table 2: Temperature for conversion of CO_2 and H_2S over Al_2O_3 supported Fe/ Zn/ Cu/ Ti catalyst with different ratios using simulated natural gas.

Catalyst	T_{100} CO_2[a] (± 0.5°C)	T_{100} H_2S (± 0.5°C)
Fe/ Zn/ Cu/ Ti (10:20:30:40)-Al_2O_3	500 (64.2 %)[b]	100
Fe/ Zn/ Cu/ Ti (5:5:40:50)-Al_2O_3	500 (75.2 %)[b]	100
Fe/ Zn/ Cu/ Ti (5:5:30:60)-Al_2O_3	500 (62.5 %)[b]	100

[a] Temperature where 100 % conversion was achieved
[b] Value in bracket is the % conversion of CO_2 at maximum studied temperature of 500 ^oC

From Table 1 and 2, it could be concluded that Fe/ Zn/ Cu (4: 16: 80)-Al_2O_3 is the most potential catalyst for conversion of CO_2. This showed that copper oxide acts as a better based element for CO_2 conversion catalyst compared to TiO. Basu *et al.* [8] have proven that the addition of TiO at a high concentration may increase the surface oxygen storage. However, this property did not assist the adsorption of CO_2 on the catalyst surface. Besides that, the interaction between Ti and H_2 is weak because H_2 prefer to adsorb on the defect TiO lattice. Thus, prevent the adsorption of H_2 during CO_2 methanation [9]. Table 2 also shows that all the three catalysts achieved 100 % conversion of H_2S at reaction temperature of 100 ^oC. However, Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al_2O_3 is considered as the most potential catalyst for desulfurization process due to its ability to convert higher percentage of H_2S at light off temperature (T_{LO} = 60 ^oC) compared to the other catalysts (not showed). Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al_2O_3 gave 96.2 % conversion of H_2S at T_{LO}; Fe/ Zn/ Cu/ Ti (10: 20: 30: 40)-Al_2O_3 catalyst gave 92.5 % while Fe/ Zn/ Cu/ Ti (5: 5: 30: 60)-Al_2O_3 gave 87.3 % conversion of H_2S at $T_{LO.}$ It has been proven that TiO could influence the dissociation of H_2S to H^+ and HS^- at the early stage due to its weak electron interaction in the *d* orbital [10].

3.1.2 In-situ reactions of CO_2 methanation and H_2S desulfurization

In order to elucidate the performance of the catalysts under *in-situ* reactions of CO_2 methanation and desulfurization condition, Al_2O_3 supported Fe/ Zn/ Cu and Fe/ Zn/ Cu/ Ti catalysts with the optimum ratio were tested using simulated natural gas environment. The selectivity and yield of CH_4 was calculated by incorporating Gas Chromatography data due to the low sensitivity of FTIR towards stretching band of CH_4.

Figure 1 shows the percentage conversion of H_2S over Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al_2O_3 catalyst is higher than Fe/ Zn/ Cu (4: 16: 80)-Al_2O_3 catalyst. The graph shows a decrease on the conversion of H_2S from room temperature to 40 ^oC. This phenomenon was assigned to the adsorption of H_2S by the catalyst. Both catalysts, completely removed H_2S at reaction temperature of 100 ^oC. On the other hand, both catalysts gave a gradual increase for the conversion of CO_2 until maximum reaction temperature of 200 ^oC. Fe/ Zn/ Cu (4: 16: 80)-Al_2O_3 catalyst showed a higher conversion of CO_2 compared to Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al_2O_3 catalyst. The catalytic activity of *in-situ* reactions over both catalysts slightly decreased compared to the individual reaction of CO_2 methanation and H_2S desulfurization.

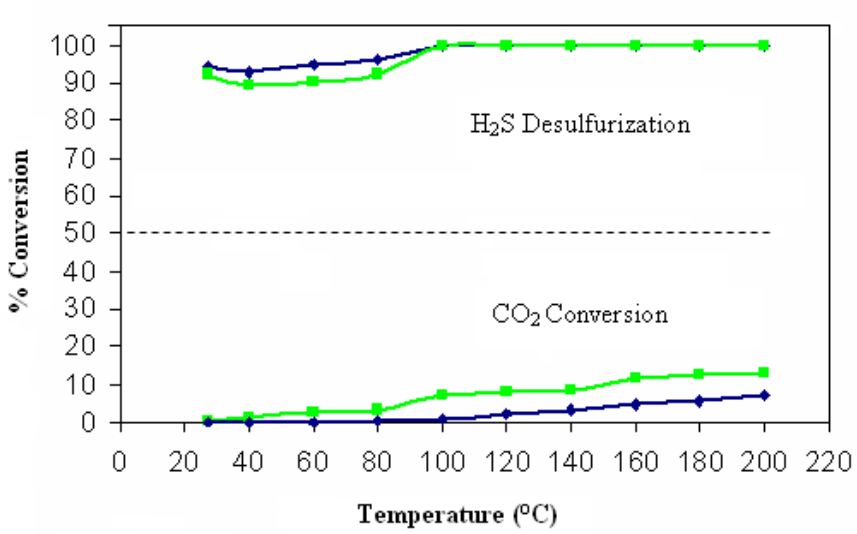

Figure 1: Percentage conversion of CO_2 and H_2S versus reaction temperature under in-situ reactions of CO_2 methanation and H_2S desulfurization over (■) Fe/ Zn/ Cu (4: 16: 80)-Al_2O_3 and (♦) Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al_2O_3 catalysts.

From Table 3, Fe/ Zn/ Cu (4: 16: 80)-Al_2O_3 catalyst yielded 0.6% and 0.7% of CH_4 at reaction temperature of 100°C and 200°C respectively. Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al_2O_3 catalyst yielded no CH_4 at 100°C and only 0.4% of CH_4 at 200°C. The selectivity of CH_4 over TiO based catalyst is considered very low. From the result, it could be considered that the conversion of CO_2 to CH_4 in this research is incomplete because higher percentage of CO formed rather than CH_4 [11]. This is due to the indirect conversion of CO_2 into C1 hydrocarbons, via intermediate formation of CO, as suggested by Silver *et al.* [12].

Table 3: Selectivity products of *in-situ* reactions of CO_2 methanation and H_2S desulfurization over the catalysts.

Catalyst	Temperature (°C)	CO_2 Conversion (%)		Unreacted CO_2 (%)
		CH_4	(CO + H_2O)	
Fe/ Zn/ Cu (4: 16: 80)-Al_2O_3	100	0.6	5.9	93.5
	200	0.7	11.3	88.0
Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al_2O_3	100	0.0	0.7	99.3
	200	0.4	6.2	93.4

* Calculation based on CO_2 detected *via* FTIR and CH_4 detected *via* GC.

3.2 Characterization of the Catalysts

3.2.1 XPS

The surface active components on the fresh and after testing (spent) catalysts of Fe/ Zn/ Cu (4: 16: 80)-Al_2O_3 and Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al_2O_3 was accomplished through XPS analysis. All data was corrected by using the binding energy of C 1s at 284.5 eV as standard. XPS analysis only detected the presence of Cu, Fe, Al

and O on the surface. Even though the EDX analysis detected the weight percentage of Zn as 0.2 % in the Fe/ Zn/ Cu (4: 16: 80)-Al_2O_3 and 0.1 % in the Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al_2O_3 catalyst, no peak assigned to Zn was detected from the deconvolution peak of Zn. This may due to the agglomeration of the other elements, which thus pushed Zn into the lattice structure of the catalyst or poisoning from carbon compound during XPS analysis [13]. In addition, the presence of Ti in the Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al_2O_3 catalyst also could not be detected due to the narrow diameter of Ti compared to Cu and Fe. It is believed that Ti was left inside the lattice structure of the catalyst. The interaction of electron from Ti was weak due to the distance of Ti inside the catalyst structure is comparably farer than those species on the surface.

The binding energy resulted from deconvolution peaks of Cu (2*p*) from the studied catalysts were tabulated in Table 4. Both fresh catalysts of Fe/ Zn/ Cu (4: 16: 80)-Al_2O_3 and Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al_2O_3 contained normal spinel compound of $CuFe_2O_4$. The normal spinel of $CuFe_2O_4$ on the Fe/ Zn/ Cu (4: 16: 80)-Al_2O_3 catalyst turned to inverse spinel structure after the catalytic testing, while it remained as normal spinel structure for the spent Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al_2O_3 catalyst. A normal spinel compound is the active site for the catalysts. Fe^{3+} made up the octahedral site while Cu^{2+} made up the tetrahedral site [14, 15]. Analysis showed that Fe/ Zn/ Cu (4: 16: 80)-Al_2O_3 and Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al_2O_3 catalysts contain spinel compound of $CuFe_2O_4$ or Fe_3O_4 that are assumed to act as active species on the surface. Fe_3O_4 is considered as the most dominant structure compared to $CuFe_2O_4$ and it is also the active site for H_2S desulfurization.

Table 4: XPS data of Cu (2*p*) for Fe/ Zn/ Cu-Al_2O_3 and Fe/ Zn/ Cu/ Ti-Al_2O_3 catalysts.

Catalyst	Weight (%)	Binding Energy (eV)[a]		ΔE_{SO}[b] (eV)	Peak Area[c] ($2p_{3/2}$)	Peak Assignment
		$2p_{3/2}$	$2p_{1/2}$			
Fe/ Zn/ Cu (4:16:80)-Al_2O_3 (fresh)	1.8	933.7	953.6	19.9	21.6	$CuFe_2O_4$ (normal spinel)
Fe/ Zn/ Cu (4:16:80)-Al_2O_3 (spent)	4.2	935.1	954.9	19.8	23.9	$CuFe_2O_4$ (inverse spinel)
Fe/ Zn/ Cu/ Ti (5:5:40:50)-Al_2O_3 (fresh)	3.6	933.6	953.5	19.9	247.6	$CuFe_2O_4$ (normal spinel)
Fe/ Zn/ Cu/ Ti (5:5:40:50)-Al_2O_3 (spent)	3.7	933.7	953.5	19.9	59.9	$CuFe_2O_4$ (normal spinel)

[a] Binding energy corrected by specific operation charge effect (284.5 eV)
[b] ΔE_{SO} (difference of 2 spin orbit) = Eb($2p_{1/2}$) - Eb($2p_{3/2}$)
[c] Peak Area = Peak Intensity x FWHM (Full Width Half Maximum)

Peaks referred to normal spinel compounds of $CuFe_2O_4$ or Fe_3O_4 appeared at binding energy of 710.1 eV ($2p_{3/2}$) and 723.7 eV ($2p_{1/2}$) for Fe/ Zn/ Cu (4: 16: 80)-Al_2O_3 catalyst, 709.7 eV ($2p_{3/2}$) and 723.2 eV ($2p_{1/2}$) for Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al_2O_3 catalyst (Table 5). Peak area of these peaks is high enough, which indicated the formation of surface Fe in a large amount. This also proved that Fe_3O_4 is a more dominant structure compared to $CuFe_2O_4$. There are another peaks at binding energy of 712.4 eV ($2p_{3/2}$) and 726.1 eV ($2p_{1/2}$) for Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al_2O_3 catalyst assigned to the Fe^{3+} bound to hydroxyl group ($^-$OH) and is in agreement with Shah *et al.* [16]. The high binding energy of these peaks is due to the high electronegativity of hydroxyl group. $^-$OH ligand is more electronegative than oxygen. The presence of hydroxyl ligand could increase the oxidation reaction over Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al_2O_3 catalyst due to its high electron density nature. Morrison [13] also proved that TiO_2 in Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al_2O_3 catalyst contributed to the presence of Fe^{3+}-OH and thus active site for the H_2S desulfurization. Thus, the adsorption process of H_2S at low temperature that may inhibit H_2S desulfurization could be avoided.

On the other hand, the spent Fe/ Zn/ Cu (4: 16: 80)-Al_2O_3 catalyst showed the deconvolution peaks of $CuFe_2O_4$ or Fe_3O_4 at binding energy of 710.1 eV ($2p_{3/2}$) and 723.7 eV ($2p_{1/2}$) but with 85.3 % reduction of peak area. This is due to the occurance of inverse spinel structure that contributed to the presence of larger amount of surface Cu. The spent catalyst of Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al_2O_3 also showed a lower peak area for the deconvolution peaks of $CuFe_2O_4$ or Fe_3O_4 at 710.5 eV ($2p_{3/2}$) and 724.1 eV ($2p_{1/2}$). The formation of CuO obstructed the distribution of Fe on the catalyst surface.

Table 5: XPS data of Fe ($2p$) for Fe/ Zn/ Cu (4:16:80)-Al_2O_3 and Fe/ Zn/ Cu/ Ti (5:5:40:50)-Al_2O_3 catalysts.

Catalyst	Weight (%)	Binding Energy (eV)[a]		ΔE_{SO}[b] (eV)	Peak Area[c] ($2p_{3/2}$)	Peak Assignment
		$2p_{3/2}$	$2p_{1/2}$			
Fe/ Zn/ Cu (4:16:80)-Al_2O_3 (fresh)	3.6	710.1	723.7	13.6	66.7	$CuFe_2O_4$/ Fe_3O_4
Fe/ Zn/ Cu (4:16:80)-Al_2O_3 (spent)	3.4	710.1	723.7	13.6	9.8	$CuFe_2O_4$/ Fe_3O_4
Fe/ Zn/ Cu/ Ti (5:5:40:50)-Al_2O_3 (fresh)	3.8	709.7	723.2	13.5	12.5	$CuFe_2O_4$/ Fe_3O_4
		712.4	726.1	13.7	6.4	Fe^{3+}-OH
Fe/ Zn/ Cu/ Ti (5:5:40:50)-Al_2O_3(spent)	2.8	710.5	724.1	13.6	10.0	$CuFe_2O_4$/ Fe_3O_4

[a] Binding energy corrected by specific operation charge effect (284.5 eV)
[b] ΔE_{SO} (difference of 2 spin orbit) = Eb($2p_{1/2}$) - Eb($2p_{3/2}$)
[c] Peak Area = Peak Intensity x FWHM (Full Width Half Maximum)

3.2.2 Nitrogen Adsorption Analysis

One of the most characteristic properties of the surface of a solid is its ability to adsorb gases and vapours. Table 6 summarized the BET surface area and BJH desorption average pore diameter of the fresh supported catalysts and after in-situ reactions testing catalysts (spent catalysts). The fresh catalysts showed relatively narrow pore size compared to the spent catalysts. It could be seen that Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al_2O_3 catalyst posseses higher surface area and narrower pore size. This was supported by Yamasaki *et al.* [17] that the addition of TiO_2 in the catalyst may increase the surface area and decrease the particle size. These features improved the H_2S desulfurization activity but not the CO_2 methanation activity. However, the catalytic activity of a particular catalyst not only depends on the BET surafce area and pore size, but also included other factors such as type of pores, shape of pores and the degree of porosity [18].

From the BET surface area analysis, the Fe/ Zn/ Cu (4: 16: 80)-Al_2O_3 catalyst showed reduction of 34 % and Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al_2O_3 catalyst showed reduction of 17 % in surface area. This reduction was possibly due to the sulfur poisoning on the surface during H_2S desulfurization. This was also proven by the Energy Dispersive X-rays Analysis (Table 7). However, the isotherm plot of the fresh and spent catalysts did not show significant difference. All the catalysts showed Type IV isotherm plot and H3 type hysteresis loop resemblance with slit-shaped pores and with non-uniform shape and size.

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Table 6: BET surface area and BJH desorption average pore diameter of the fresh supported catalysts and after in-situ reactions testing catalysts

Catalyst	S_{BET} ($m^2 g^{-1}$)	d (nm)
Fe/ Zn/ Cu (4:16:80)-Al_2O_3 (fresh)	184.8	5.1
Fe/ Zn/ Cu (4:16:80)-Al_2O_3 (spent)	121.6	7.1
Fe/ Zn/ Cu/ Ti (5:5:40:50)-Al_2O_3 (fresh)	259.2	2.6
Fe/ Zn/ Cu/ Ti (5:5:40:50)-Al_2O_3 (spent)	215.6	3.2

Table 7: Elemental composition of Fe/ Zn/ Cu (4: 16: 80)-Al_2O_3 and Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al_2O_3 catalysts analyzed by Energy Dispersive X-rays Analysis.

Catalyst	Condition	Atomic Weight Percentage (%)						
		Ti	Cu	Zn	Fe	S	Al	O
Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al_2O_3	Before testing	4.90	3.88	0.48	0.47	0.00	40.41	49.86
	After testing	4.82	3.80	0.43	0.41	1.43	39.94	49.17
	After regeneration	4.89	3.87	0.46	0.45	0.00	40.22	50.11
Fe/ Zn/ Cu (4: 16: 80)-Al_2O_3	Before testing	0.00	14.83	3.68	0.74	0.00	49.12	31.63
	After testing	0.00	14.75	3.64	0.70	2.32	48.64	29.95
	After regeneration	0.00	14.84	3.65	0.73	0.00	50.06	30.72

4. Conclusion

The optimum ratio for Al_2O_3 supported CuO based catalyst obtained was Fe/ Zn/ Cu = 4: 16: 80, while for TiO based catalyst was Fe/ Zn/ Cu/ Ti = 5: 5: 40: 50. Both of the catalysts completely converted H_2S to elemental sulfur at reaction temperature of 100 ^oC. The aim to obtain high H_2S desulfurization rate at low temperature was achieved. The introduction of Fe, Zn, Cu and Ti intended to catalyze the CO_2/ H_2 methanation reaction in the presence of H_2S proved ineffective in this case. However, it has been observed that Fe/ Zn Cu (4: 16: 80)-Al_2O_3 catalyst showed a higher conversion and also CH_4 formation compared to Fe/ Zn/ Cu/ Ti (5: 5: 40: 50)-Al_2O_3. The catalytic activities of *in-situ* reactions over both catalysts showed a slightly decrease compared to the individual reaction of CO_2 methanation and H_2S. Therefore, further efforts are needed in the future work in the attempt to obtain catalysts that may increase the conversion rate of CO_2 and H_2S simultaneously.

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